

# Structures and energetics of hydrocarbon molecules in a wide hydrogen chemical potential range

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## Abstract

We report a collection of lowest-energy structures of hydrocarbon molecules  $C_mH_n$  ( $m=1-18$ ;  $n=0-2m+2$ ). The structures are examined within a wide hydrogen chemical potential range. The genetic algorithm combined with Brenner's empirical potential is applied for the search. The resultant low-energy structures are further studied by *ab initio* quantum chemical calculations. The lowest-energy structures are presented with several additional low-energy structures for comparison. The results are expected to provide useful information for some unresolved astronomical spectra and the nucleation of growth of nano-diamond film.

## INTRODUCTION

Hydrocarbon molecules, especially polycyclic aromatic hydrocarbons (PAHs), have received much attention for the broad astronomical interests. PAHs were proposed to be the possible carriers of the unidentified infrared (IR) emission bands[1], the interstellar ultraviolet (UV) extinction curve[2, 3] and the diffuse interstellar bands[4–6]. Though quite a few achievements have been made in recent years[7, 8], the PAH hypotheses are not fully addressed. Possible different charged states of PAHs may increase its complexity, however, one intrinsic difficulty could be stemmed from the very complicated phase space of hydrocarbons due to the enormous bonding ability of carbon. Furthermore, the phase space is also dependent of the hydrogen chemical potential, as the observed IR spectra may be different in different interstellar environments[8].

In this paper, we focus on providing a collection of lowest-energy structures for  $C_mH_n$  ( $m=1-18$ ;  $n=0-2m+2$ ) in a wide hydrogen chemical potential range with the aid of a series of unbiased global searches. Our results are expected to be helpful for addressing the above PAH hypotheses. Moreover, since the most abundant reactive elements in the cosmos are carbon and hydrogen, our database should be helpful in elucidating the evolution of carbon from its birthsite in circumstellar shells through interstellar medium, which may be related to astrobiology ultimately[8]. Useful information for a better understanding of the mechanism of nucleation and growth for nano-diamond films may also be extracted from our results[9, 10].

## COMPUTATIONAL METHODS

The global structure optimization is based on our early developed genetic algorithm (GA)[11]. An illustrative online version of the code for the optimization of a two-dimensional map has been published in nanohub[12]. Each GA run is started with a randomly generated pool with typically 100 structures which are relaxed to local minimum with Brenner’s empirical potential[13]. The size of pool may vary with different investigated systems. The random generation of the pool may be guided by some physical intuition. The evolution of the pool is realized by performing mating operations. Each operation includes randomly selecting two structures (parents) from the pool, cutting them with a common plane randomly

selected, then combining the opposite parts relative to the cutting plane from the parents to create a new structure (child). The child structure is relaxed within Brenner’s model[13]. The decision of replacing the highest-energy structure in the pool with the child structure is based on energy criterion  $f$  defined as

$$f = (E - n_H \mu_H) / n_C \quad (1)$$

where  $E$  is the total energy of the cluster with  $n_H$  hydrogen atoms and  $n_C$  carbon atoms.  $n_C$  is fixed for each GA run, while  $n_H$  may be varied in a physically reasonable range.  $\mu_H$  is the hydrogen chemical potential, which may be fixed to some particular value(s)[14] or a range of interest. In this work, we are interested in a wide hydrogen chemical potential range, which is taken as (-6eV, 0) in Brenner’s model, i.e., the lowest (highest)-hydrogen chemical potential value guarantees that the optimum molecules are pure carbon clusters (alkanes). In practice  $\mu_H$  is uniformly sampled in this chemical potential range by step size of 0.05 eV. The mating operations performed with parents of different number of hydrogen atoms may provide a superior sampling of the potential energy landscape[14]. Each GA run has typically 10000 generations with 15 random pairs of molecules mated for each generation. At the end of each GA run, the candidate structures are further relaxed by *ab initio* quantum chemistry method.

Recently it has been pointed out that density functional theory (DFT) is unreliable for computing hydrocarbon isomer energy differences[15, 16]. Fig.1 shows the correlation between experimental isomer energy differences and those calculated at second order Møller–Plesset perturbation theory (MP2), DFT-B3LYP, DFT-PBEOP levels with basis set of 6-31(d) for 9  $C_6H_{10}$ , 7  $C_6H_{12}$ , 5  $C_6H_{14}$ , 4  $C_7H_{14}$  and 9  $C_7H_{16}$  molecules. MP2 gives a best correlation with the experiments, especially for the low-energy molecules. Hence all the candidate hydrocarbon structures in the final pool from GA are relaxed at level of MP2/6-31G(d) using GAMESS package[17].

## RESULTS

We systematically searched for the lowest energy structures of hydrocarbon molecules  $C_m H_n$  ( $m=1-18$ ;  $n=0-2m+2$ ) in a wide hydrogen chemical potential range of (-6eV, 0). Fig.2-14 show MP2-relaxed lowest-energy structures from our unbiased global searches. Sev-

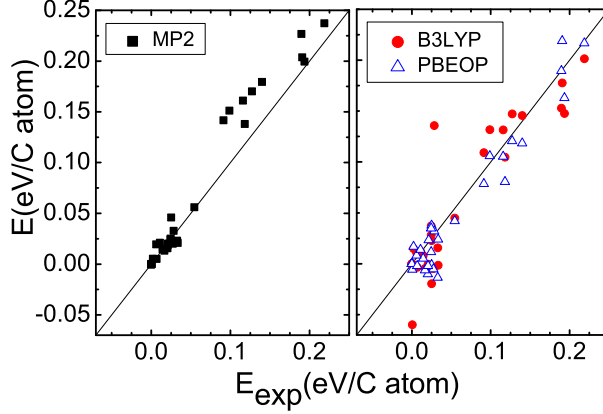


FIG. 1: (Color online) Computed isomer energy differences at MP2 (black square), DFT-B3LYP (red circle) and DFT-PBEOP (blue triangle) level versus experimental values for 34 hydrocarbon molecules.

eral low-energy isomers were also shown for comparison. The ground state geometries of pure carbon clusters have been extensively studied and reviewed[18]. It usually requires higher level of quantum chemistry calculations to determine the fine structures and energy differences between the isomers. In this paper we focus on providing the lowest-energy hydrocarbon clusters in various hydrogen chemical potentials and the lowest-energy pure carbon clusters are intended to be chosen as reference systems. Nevertheless, the general features (i.e., chain or ring structure) of the ground state geometries of pure carbon clusters are consistent with the results in the literature[18, 19].



Fig. 2 shows the lowest energy structures with a backbone of 6 carbon atoms in the full hydrogen chemical potential range. The relative energy  $E_0$  associated with each structure is defined as

$$E_0 = E_{C_nH_m} - E_{C_n} - mE_H \quad (2)$$

where  $E_{C_nH_m}$ ,  $E_{C_n}$  and  $E_H$  are the total energies of the hydrocarbon  $C_nH_m$ , pure carbon cluster  $C_n$  and hydrogen atom  $H$ , with  $E_H = -1.356\text{eV}$ . The energies are evaluated at MP2/6-31G(d) level. The pure  $C_6$  cluster is chosen as the reference point. In this C6 group, the lowest-energy hydrocarbon structures in the hydrogen chemical

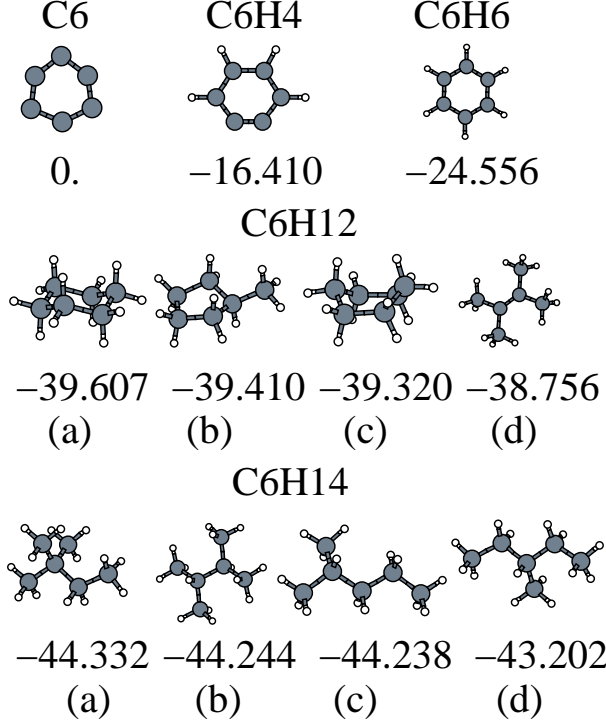


FIG. 2: 11 lowest energy structures of  $C_6H_m$  in full hydrogen chemical potential range. The number below each structure is the relative energy  $E_0$  in unit of eV. 11 lowest energy structures of  $C_6H_m$  in full hydrogen chemical potential range. The number below each structure is the relative energy  $E_0$  in unit of eV.

potential range of  $(-6.000eV, -4.155eV)$ ,  $(-4.155eV, -4.073eV)$ ,  $(-4.073eV, -2.473eV)$ ,  $(-2.473eV, -2.363eV)$ ,  $(-2.363eV, 0)$  are  $C_6$  (chain),  $C_6H_4$  (Benzyne),  $C_6H_6$  (Benzene),  $C_6H_{12}$  (a, Cyclohexane) and  $C_6H_{14}$  (a, 2,2-Dimethylbutane), respectively. Several low energy isomers in  $C_6H_{12}$  and  $C_6H_{14}$  group are also shown for reference. Cyclohexane with boat conformation  $C_6H_{12}(c)$  is  $0.287eV$  higher in energy than Cyclohexane with chair conformation  $C_6H_{12}(a)$ , close to the experimental result  $0.238\text{ eV}$ [20]. Methylcyclopentane  $C_6H_{12}(b)$  is in between and  $0.197\text{ eV}$  higher than  $C_6H_{12}(a)$ , close to experimental value  $0.177\text{ eV}$ [21].  $C_6H_{12}(d)$  is rather high in energy because of its diradical structure. The energy orders of the four alkane isomers are correctly predicted by MP2 as compared with experimental results although the energy difference can be quite small[21].

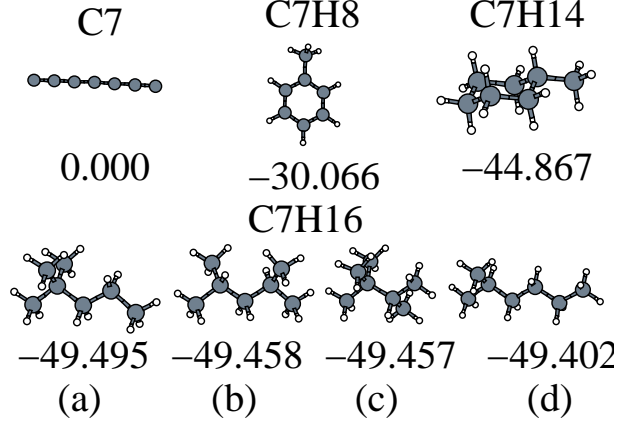


FIG. 3: 7 lowest energy structures of  $C_7H_m$  in full hydrogen chemical potential range. The number below each structure is the relative energy  $E_0$  in unit of eV.

$$C_7H_m$$

Fig. 3 shows the lowest energy structures with a backbone of 7 carbon atoms in the full hydrogen chemical potential range. In this  $C_7$  group, the lowest-energy hydrocarbon structures in hydrogen chemical potential range of  $(-6.000eV, -3.758eV)$ ,  $(-3.758eV, -2.467eV)$ ,  $(-2.467eV, -2.314eV)$ ,  $(-2.314eV, 0)$  are  $C_7$  (chain),  $C_7H_8$  (Methylbenzene),  $C_7H_{14}$  (Methylcyclohexane) and  $C_7H_{16}$  (a,2,2-Dimethylpentane), respectively. From  $C_6$  to  $C_7$  group, the system mainly choose to add one methyl to the dominant lowest energy hydrocarbon molecules (i.e., Benzene and Cyclohexane) and exhibit four different lowest energy chemical compositions in the whole hydrogen chemical potential range. The alkane subgroup is different and still the one with one end methyl pair has lowest energy, in consistence with experiment[21].

$$C_8H_m$$

Fig. 4 shows the lowest energy structures with a backbone of 8 carbon atoms in the full hydrogen chemical potential range. In this  $C_8$  group, the lowest-energy hydrocarbon structures in hydrogen chemical potential range  $(-6.000eV, -4.243eV)$ ,  $(-4.243eV, -2.905eV)$ ,  $(-2.905eV, -2.459eV)$ ,  $(-2.459eV, -2.266)$ ,  $(-2.266eV, 0)$  are  $C_8$  (ring),  $C_8H_6$  (a,Ethynylbenzene),  $C_8H_{10}$  (a,1,2-Dimethylbenzene),  $C_8H_{16}$  (a,cis-1,3-

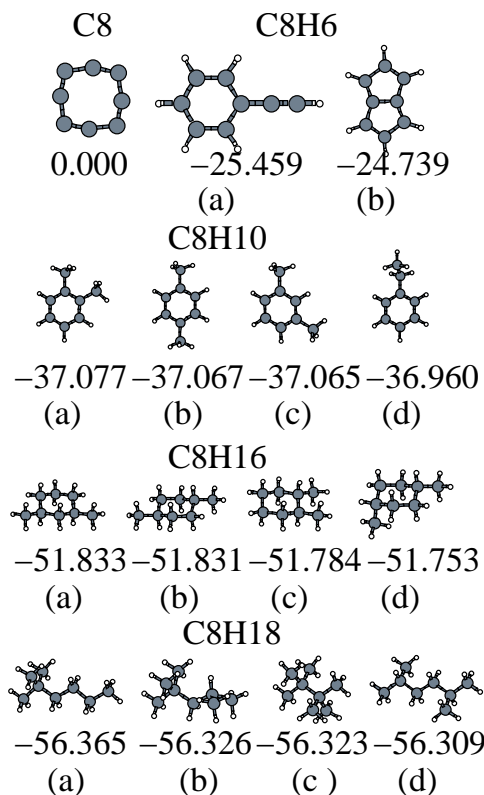


FIG. 4: 15 lowest energy structures of  $C_8H_m$  in full hydrogen chemical potential range. The number below each structure is the relative energy  $E_0$  in unit of eV.

Dimethylcyclohexane) and  $C_8H_{18}$  (a,2,2-Dimethylhexane), respectively. Ethynylbenzene has lower energy than  $C_8H_6$ (b,Pentalene) because of its conjugated bond configuration. The first three low energy Benzene-based isomers in C8H10 subgroup are very close in energy. MP2-level calculations can not correctly predict the energy orders between them and favor 1,2-Dimethylbenzene. In contrast, gas phase thermochemistry measurement shows that  $C_8H_{10}$  (c,1,3-Dimethylbenzene) is 0.018 eV lower in energy than 1,2-Dimethylbenzene[21]. On the other hand, MP2 predicts that  $C_8H_{10}$  (d,Ethylbenzene) is higher in energy than the Dimethylbenzenes in agreement with experiment[21]. For the C8H16 subgroup, MP2 also predicts that Dimethylcyclohexanes have lower energies than Ethylcyclohexane and the energy differences between Dimethylcyclohexanes can be very small. In the alkane subgroup, the one with one end methyl pair is still the lowest energy isomer.

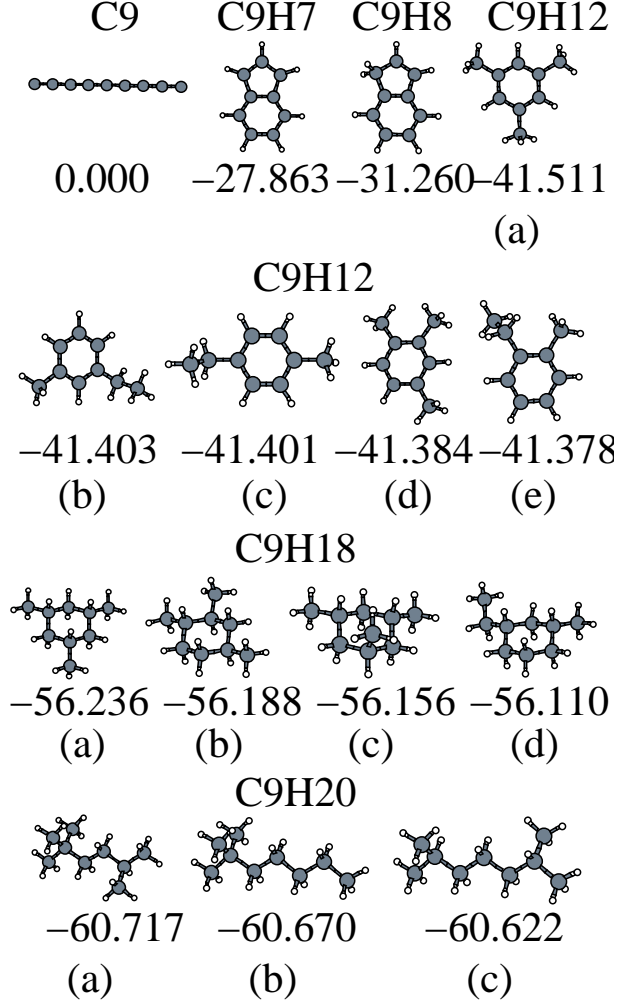


FIG. 5: 15 lowest energy structures of  $C_9H_m$  in full hydrogen chemical potential range. The number below each structure is the relative energy  $E_0$  in unit of eV.

$$C_9H_m$$

Fig. 5 shows the lowest energy structures with a backbone of 9 carbon atoms in the full hydrogen chemical potential range. In this C9 group, the lowest-energy hydrocarbon structures in hydrogen chemical potential range  $(-6.000eV, -3.981eV)$ ,  $(-3.981eV, -3.397eV)$ ,  $(-3.397eV, -2.563eV)$ ,  $(-2.563eV, -2.454eV)$ ,  $(-2.454eV, -2.240eV)$ ,  $(-2.20eV, 0)$  are  $C_9$  (chain),  $C_9H_7$ ,  $C_9H_8$  (indene),  $C_9H_{12}$  (a,1,2,5-Trimethylbenzene),  $C_9H_{18}$  (1,3,5-Trimethylcyclohexane) and  $C_9H_{20}$  (a,2,2,5-Trimethylhexane), respectively. The group shows more ground state chemical compositions in the full hydrogen chemical potential range. MP2 predicts that the isomer with 1,3,5-Trimethyl has the lowest energy in both C9H12



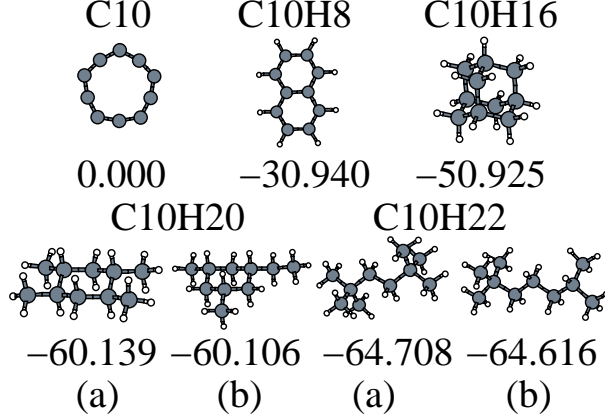


FIG. 6: 7 lowest energy structures of  $C_{10}H_m$  in full hydrogen chemical potential range. The number below each structure is the relative energy  $E_0$  in unit of eV.

and  $C_9H_{18}$  subgroups due to maximal reduction of the repulsion energy between the hydrogen atoms. The ground state geometry of the alkane subgroup is predicted to have three methyls in accordance with experiment[21].

$$C_{10}H_m$$

Fig. 6 shows the lowest energy structures with a backbone of 10 carbon atoms in the full hydrogen chemical potential range. In this  $C_{10}$  group, the lowest-energy hydrocarbon structures in hydrogen chemical potential range  $(-6.000eV, -3.868eV)$ ,  $(-3.868eV, -2.498eV)$ ,  $(-2.498eV, -2.303eV)$ ,  $(-2.303eV, -2.285eV)$ ,  $(-2.285eV, 0)$  are  $C_{10}$  (ring),  $C_{10}H_8$  (Naphthalene),  $C_{10}H_{16}$  (Adamantane),  $C_{10}H_{20}$  (a,trans-1,2,4,5-Tetramethylcyclohexane) and  $C_{10}H_{22}$  (a,2,2,5,5-Tetramethylhexane), respectively. Interestingly, the smallest 3D fragment of diamond (i.e., Adamantane) appears as a ground state geometry in the group. The corresponding chemical potential range is quite narrow though. The 2D cyclohexane-based structure is still present. The isomer with methy pair at both ends is predicted to have the ground state geometry in the alkane subgroup.

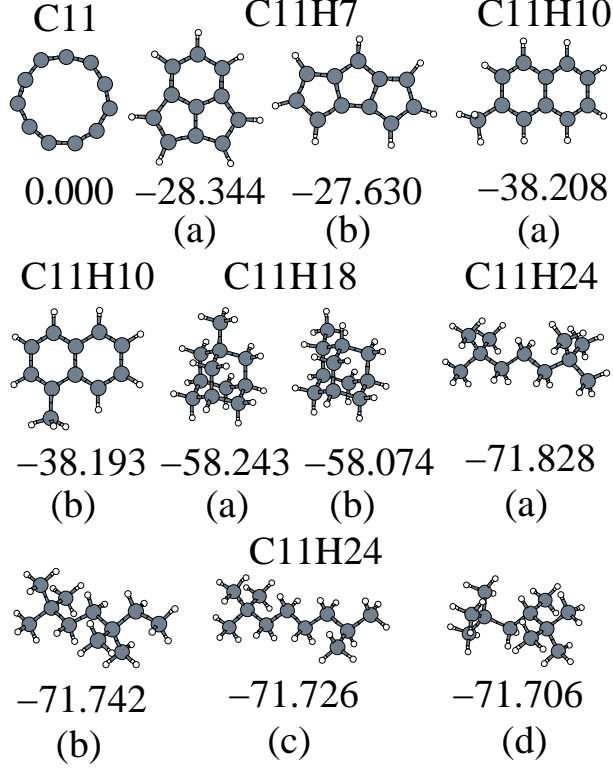


FIG. 7: 11 lowest energy structures of  $C_{11}H_m$  in full hydrogen chemical potential range. The number below each structure is the relative energy  $E_0$  in unit of eV.

$$C_{11}H_m$$

Fig. 7 shows the lowest energy structures with a backbone of 11 carbon atoms in the full hydrogen chemical potential range. In this C11 group, the lowest-energy hydrocarbon structures in hydrogen chemical potential range  $(-6.000\text{eV}, -4.049\text{eV})$ ,  $(-4.049\text{eV}, -3.288\text{eV})$ ,  $(-3.288\text{eV}, -2.504\text{eV})$ ,  $(-2.504\text{eV}, -2.264\text{eV})$ ,  $(-2.264\text{eV}, 0)$  are  $C_{11}$  (ring),  $C_{11}H_7$ ,  $C_{11}H_{10}$  (a,2-Methylnaphthalene),  $C_{11}H_{18}$  (a,1-Methyladamantane) and  $C_{11}H_{24}$  (a,2,2,5,5-Tetramethyheptane), respectively. The energy order of the isomers in C11H10 subgroup is correctly predicted by MP2 compared with experiment although the energy difference is tiny[21]. MP2 favors the growth of one methyl at the monohydrogen site and predicts that 1-Methyladamantane is 0.169 eV lower in energy than  $C_{11}H_{18}$  (b,2-Methyladamantane), close to the experimental value of 0.206 eV[21]. One may also observe that the 2D cyclohexane-based structure disappears in the ground state geometries of the hydrocarbons with carbon number larger than ten. Thus we observe a crossover between

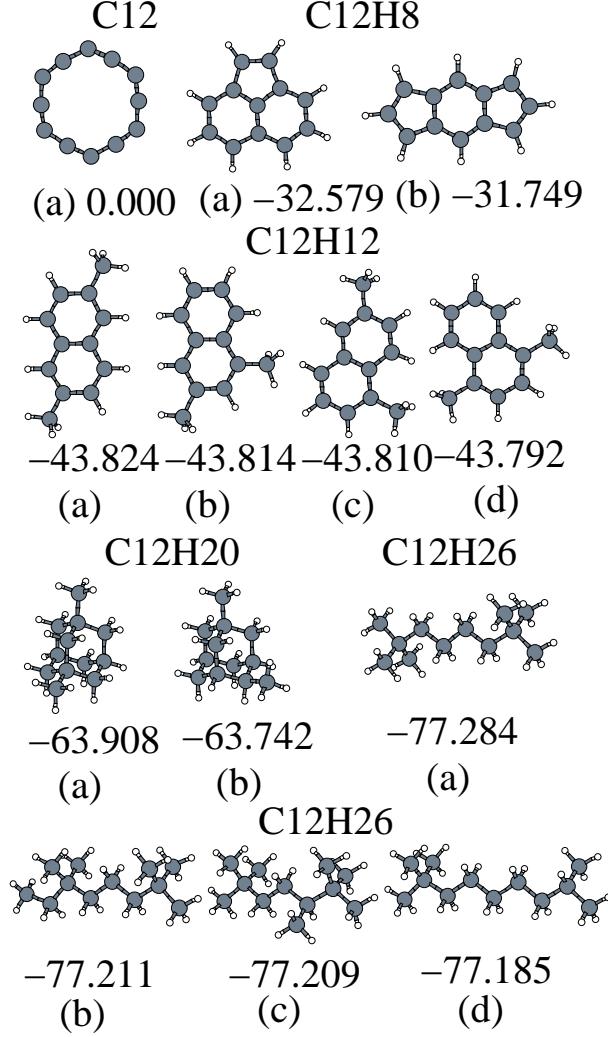


FIG. 8: 13 lowest energy structures of  $C_{12}H_m$  in full hydrogen chemical potential range. The number below each structure is the relative energy  $E_0$  in unit of eV.

populations of 2D cyclohexane-based structure and 3D diamond fragment with increasing size of hydrocarbon. The ground state isomer in the alkane subgroup is still predicted to the one with methyl pair at both ends.

$$C_{12}H_m$$

Fig. 8 shows the lowest energy structures with a backbone of 12 carbon atoms in the full hydrogen chemical potential range. In this C12 group, the lowest-energy hydrocarbon structures in hydrogen chemical potential range  $(-6.000\text{eV}, -4.198\text{eV})$ ,  $(-4.198\text{eV}, -2.561\text{eV})$ ,

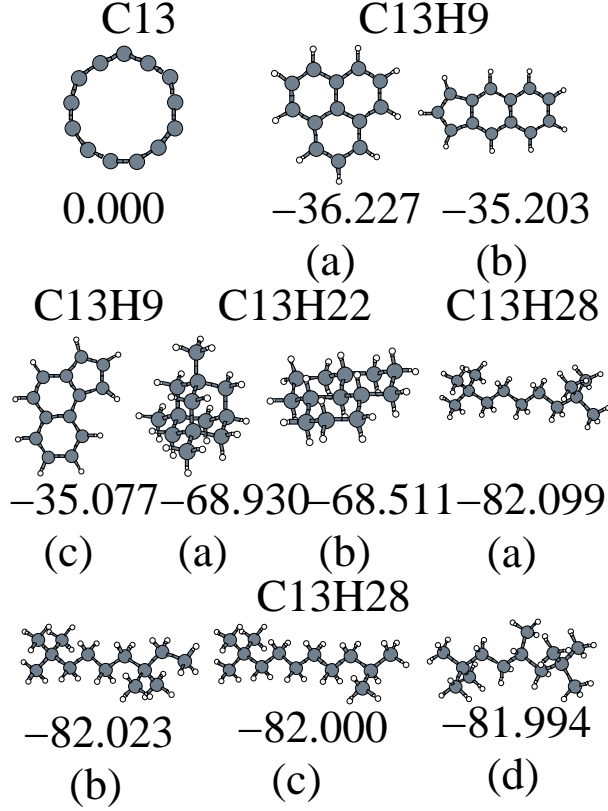


FIG. 9: 10 lowest energy structures of  $C_{13}H_m$  in full hydrogen chemical potential range. The number below each structure is the relative energy  $E_0$  in unit of eV. 10 lowest energy structures of  $C_{13}H_m$  in full hydrogen chemical potential range. The number below each structure is the relative energy  $E_0$  in unit of eV.

$(-2.561\text{eV}, -2.511\text{eV})$ ,  $(-2.511\text{eV}, -2.230\text{eV})$ ,  $(-2.230\text{eV}, 0)$  are  $C_{12}$  (ring),  $C_{12}H_8$  (Acenaphthylene),  $C_{12}H_{12}$  (a,2,6-Dimethylnaphthalene),  $C_{12}H_{20}$  (a,1,3-Dimethyladamantane) and  $C_{12}H_{26}$  (a,2,2,7,7-Tetramethyloctane), respectively. Similar rules as mentioned above can be applied here: 2,6-Dimethylnaphthalene is the lowest energy isomer because of the maximal reduction of the repulsion energy between the hydrogen atoms; monohydrogen site is the preferred site to grow methyl on adamantane; the isomer with methyl pair at both ends is still lowest in energy in the alkane subgroup.

### $C_{13}H_m$

Fig. 9 shows the lowest energy structures with a backbone of 13 carbon atoms in the full hydrogen chemical potential range. In this C13 group, the lowest-energy hydrocarbon structures in hydrogen chemical potential range  $(-6.000eV, -4.025eV)$ ,  $(-4.025eV, -2.516eV)$ ,  $(-2.516eV, -2.195eV)$ ,  $(-2.195eV, 0)$  are  $C_{13}$  (ring),  $C_{13}H_9$  (Phenalene),  $C_{13}H_{22}$  (a,1,3,5-Trimethylnaphthalene) and  $C_{13}H_{28}$  (a,2,2,8,8-Tetramethylnonane), respectively. Phenalene is the lowest energy isomer in C13H9 subgroup due to its closely packed aromatic rings. 1,3,5-Trimethylnaphthalene is predicted to be much lower in energy than  $C_{13}H_{22}$ (b,dodecahydro-1H-Phenalene). The ground state structure in the alkane subgroup still keeps the single carbon chain with methyl pair at both ends.

### $C_{14}H_m$

Fig. 10 shows the lowest energy structures with a backbone of 14 carbon atoms in the full hydrogen chemical potential range. In this C14 group, the lowest-energy hydrocarbon structures in hydrogen chemical potential range of  $(-6.000eV, -4.113eV)$ ,  $(-4.113eV, -3.283eV)$ ,  $(-3.283eV, -2.515eV)$ ,  $(-2.515eV, -2.399eV)$ ,  $(-2.399eV, -2.163eV)$ ,  $(-2.163eV, 0)$  are  $C_{14}$  (ring),  $C_{14}H_8$  (Cyclopent[fg]acenaphthylene),  $C_{14}H_{10}$  (a,Phenanthrene),  $C_{14}H_{20}$  (a,Diamantane),  $C_{14}H_{24}$  (a,1,3,5,7-Tetramethyladamantane) and  $C_{14}H_{30}$  (a,2,2,5,8,8-penmethylnonane), respectively. Contrary to the rule of maximal reduction of repulsion energy between hydrogen atoms, Phenanthrene is correctly predicted to be 0.283 eV lower in energy than  $C_{14}H_{10}$ (b,Anthracene), comparable to the experimental result of 0.216 eV. A bigger diamond fragment (Diamantane) appears as ground state structure in a narrow hydrogen chemical potential range. The fifth methyl appears in the middle of the carbon chain besides methyl pair at both ends of the lowest energy isomer in the alkane subgroup.

### $C_{15}H_m$

Fig. 11 shows the lowest energy structures with a backbone of 15 carbon atoms in the full hydrogen chemical potential range. In this C15 group, the lowest-energy hydrocarbon structures in hydrogen chemical potential range of  $(-6.000eV, -4.239eV)$ ,  $(-4.239eV, -2.729eV)$ ,  $(-2.720eV, -2.519eV)$ ,  $(-2.519eV, -2.243eV)$ ,  $(-2.243eV, 0)$  are

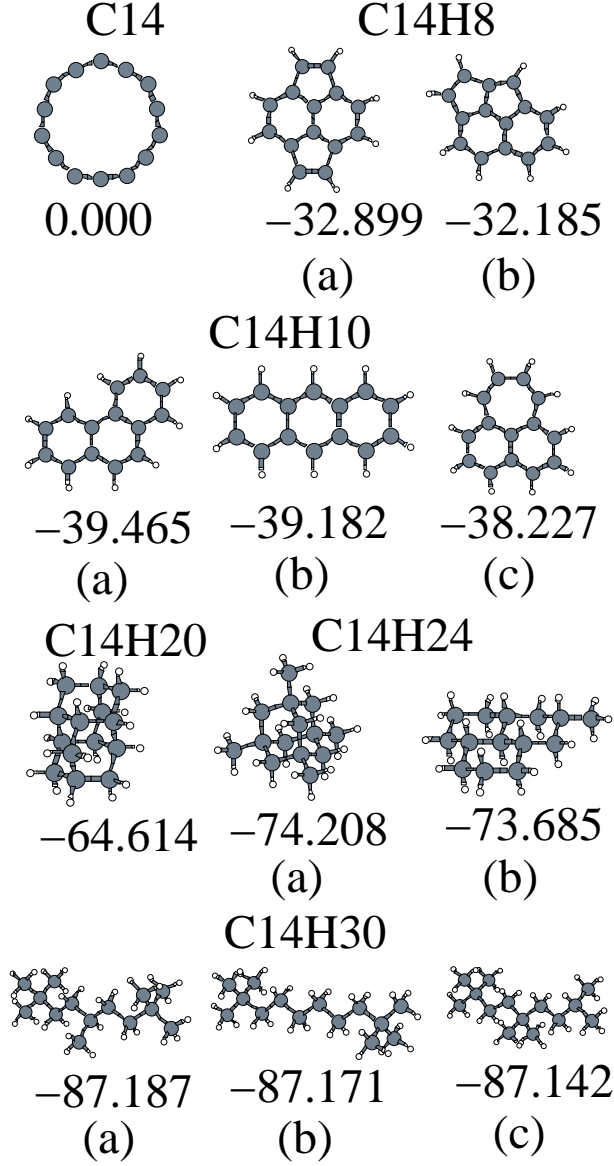


FIG. 10: 12 lowest energy structures of  $C_{14}H_m$  in full hydrogen chemical potential range. The number below each structure is the relative energy  $E_0$  in unit of eV.

$C_{15}$  (ring),  $C_{15}H_9$  (a),  $C_{15}H_{12}$  (3-Methylphenanthrene),  $C_{15}H_{22}$  (a,3-Methyldiadamantane) and  $C_{15}H_{32}$  (a,2,2,5,5,8,8-Hexamethylnonane), respectively.  $C_{15}H_9$  (a) is predicted to be the lowest energy isomer due to its compact structure and minimal influence of the five fold ring. Methyl is still preferred to grow at the monohydrogen site of diadamantane. Three pairs of methyls are distributed symmetrically on the carbon chain in the ground state structure of alkane subgroup.

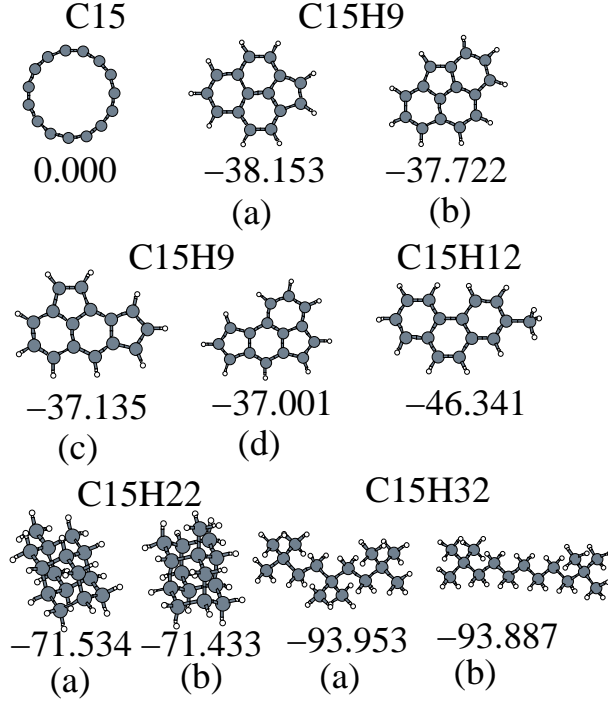


FIG. 11: 10 lowest energy structures of  $C_{15}H_m$  in full hydrogen chemical potential range. The number below each structure is the relative energy  $E_0$  in unit of eV.

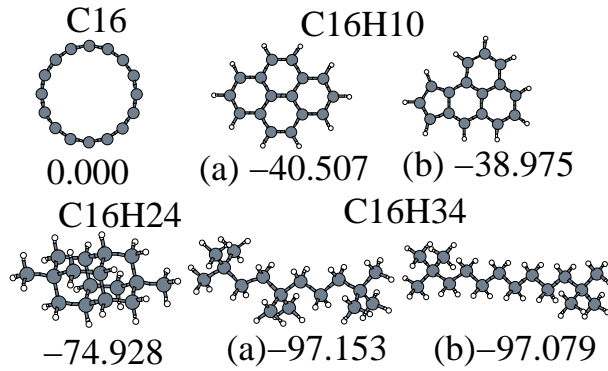


FIG. 12: 6 lowest energy structures of  $C_{16}H_m$  in full hydrogen chemical potential range. The number below each structure is the relative energy  $E_0$  in unit of eV.

$$C_{16}H_m$$

Fig. 12 shows the lowest energy structures with a backbone of 16 carbon atoms in the full hydrogen chemical potential range. In this C16 group, the lowest-energy hydrocarbon structures in hydrogen chemical potential range  $(-6.000\text{eV}, -4.051\text{eV})$ ,  $(-4.051\text{eV}, -2.459\text{eV})$ ,

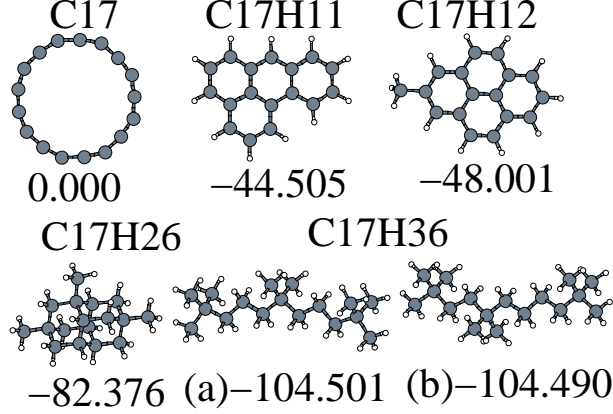


FIG. 13: 6 lowest energy structures of  $C_{17}H_m$  in full hydrogen chemical potential range. The number below each structure is the relative energy  $E_0$  in unit of eV.

$(-2.459\text{eV}, -2.223\text{eV})$ ,  $(-2.223\text{eV}, 0)$  are  $C_{16}$  (ring),  $C_{16}H_{10}$  (a,Pyrene),  $C_{16}H_{24}$ , and  $C_{16}H_{34}$  (a,2,2,5,5,9,9-Hexamethyloctane), respectively.

#### $C_{17}H_m$

Fig. 13 shows the lowest energy structures with a backbone of 17 carbon atoms in the full hydrogen chemical potential range. In this C17 group, the lowest-energy hydrocarbon structures in hydrogen chemical potential range of  $(-6.000\text{eV}, -4.046\text{eV})$ ,  $(-4.046\text{eV}, -3.496\text{eV})$ ,  $(-3.496\text{eV}, -2.456\text{eV})$ ,  $(-2.456\text{eV}, -2.213\text{eV})$ ,  $(-2.213\text{eV}, 0)$  are  $C_{17}$  (ring),  $C_{17}H_{11}$ ,  $C_{17}H_{12}$  (2-Methylpyrene),  $C_{17}H_{26}$ , and  $C_{17}H_{36}$  (a,2,2,6,6,10,10-Hexamethylundecane), respectively.

#### $C_{18}H_m$

Fig. 14 shows the lowest energy structures with a backbone of 18 carbon atoms in the full hydrogen chemical potential range. In this C18 group, the lowest-energy hydrocarbon structures in hydrogen chemical potential range  $(-6.000\text{eV}, -4.377\text{eV})$ ,  $(-4.377\text{eV}, -2.564\text{eV})$ ,  $(-2.564\text{eV}, -2.506\text{eV})$ ,  $(-2.506\text{eV}, -2.234\text{eV})$ ,  $(-2.234\text{eV}, 0)$  are  $C_{18}$  (ring),  $C_{18}H_{10}$  (a),  $C_{18}H_{14}$  (2,7-Dimethylpyrene),  $C_{18}H_{24}$  (Diamantane) and  $C_{18}H_{38}$  (a,2,2,5,5,11,11-Hexamethyldodecane), respectively. Similar empirical rules are observed in C16-C18 groups: Poly-aromatic rings tend to form compact structure; Methyl favors



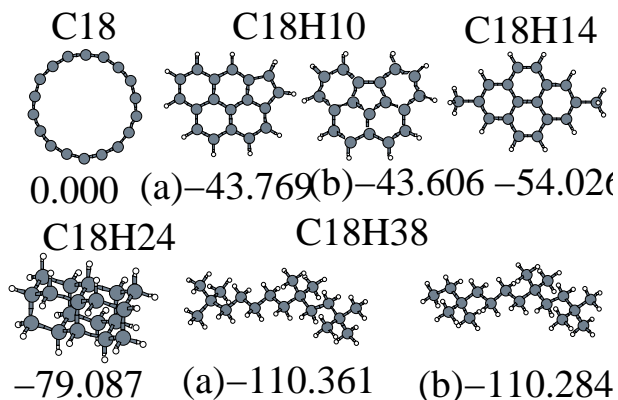


FIG. 14: 7 lowest energy structures of  $C_{18}H_m$  in full hydrogen chemical potential range. The number below each structure is the relative energy  $E_0$  in unit of eV.

the monohydrogen site in diamond fragment structure; ground state structure of alkane subgroup favors methyl pairs spaced by at least two carbon atoms over the main carbon chain.

## CONCLUSION

An unbiased evolution-based optimization method combined with Brenner's empirical potential is used to search for ground state structures of hydrocarbon molecules in a wide hydrogen chemical potential range. The resultant structures are further sorted by quantum chemical calculations at MP2 level. The collection of lowest energy structures of hydrocarbon molecules  $C_mH_n$  ( $m=1-18$ ;  $n=0-2m+2$ ) is presented. A crossover between populations of 2D cyclohexane-based structure and 3D diamond fragment with increasing number of carbon atoms of the hydrocarbon molecules is demonstrated. Besides the PAH compounds, we also show that PAH with methyls can also be important in the interstellar medium. The spectra of the PAH compounds and how are they affected by the various configurations of the radicals (e.g., methyl) are worthy of further studying.

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